PERFORMANCE ANALYSIS OF A DOWNDRAFT AND FLUIDIZED BED BIOMASS GASIFICATION USING THERMODYNAMIC EQUILIBRIUM MODEL

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ABSTRACT

Gasification is a process of producing fuel gas or synthesis gas from biomass using gasifier. The gas produced through this process particularly hydrogen will be utilized further as an input for power generation in order to produce energy. Due to the environmental concern and sustainability issues, energy from biomass has become one of the most promising renewable sources of energy. Current research points to improve the gasifier performance in order to elevate more economical product from the gasifier. For this purpose, the thermodynamic equilibrium model can be employed to predict the gas composition and to optimize important gasifier parameters for various kinds of gasifiers as well as utilizing various types of biomasses. In this work, the biomasses consisting of wood, rice husk, saw dust and empty fruit brunch are selected considering their low cost and availabilities as an abundant resource in Malaysia. These biomass sources are then served as the inputs for downdraft and fluidized bed gasifier for producing the hydrogen gas and through this study, the performance analysis in terms of the optimal parameters and gas output composition are then carried out. Here the air is used as an input reactant for downdraft gasifier and the fluidized bed gasifier is employing steam for the gasification process. In this work, the model validation is carried out first where the gas composition data obtained from thermodynamic equilibrium model show good agreement with experimental result from Zainal et al. (2001) for downdraft gasifier employing wood and Karmakar and Datta (2011) for fluidized bed gasifier using rice husk. Afterwards the performance analysis is performed to investigate the optimum parameters for downdraft and fluidized bed gasifiers. Based on this analysis, the optimum parameters obtained are at temperature 770^0C with moisture content of 0.2 and steam biomass ratio 1.32, the hydrogen gas produced from wood, rice husk, sawdust and empty fruit bunch in downdraft gasifier is 16.38%, 17.02%, 16.30% and 50.12 % respectively, while in the fluidized bed gasifier is 38.75%, 50.00%, 73.30% and 71.77% respectively. The result of the performance analysis shows that the fluidized bed gasifier is more efficient than downdraft gasifier in term of hydrogen gas production.

ABSTRAK

Pengegasan adalah satu proses untuk menghasilkan gas bahan api atau gas sintesis daripada biomas menggunakan penggas. Gas yang dihasilkan melalui proses ini terutamanya hidrogen akan digunakan lagi sebagai input bagi penjanaan kuasa untuk menghasilkan tenaga. Disebabkan oleh kebimbangan dan kemampanan isu-isu alam sekitar, tenaga daripada biojisim telah menjadi salah satu sumber yang boleh diperbaharui yang paling menjanjikan tenaga. Titik penyelidikan semasa untuk meningkatkan prestasi penggas untuk meningkatkan produk lebih menjimatkan daripada penggas. Untuk tujuan ini, model keseimbangan termodinamik boleh digunakan untuk meramalkan komposisi gas dan untuk mengoptimumkan parameter Penggas penting untuk pelbagai jenis gasifiers serta menggunakan pelbagai jenis biomasses. Dalam karya ini, biomas yang terdiri daripada kayu, sekam padi, habuk papan dan buah tandan kosong dipilih memandangkan cos yang rendah dan sumber didapati di Malaysia. Sumber-sumber biomas kemudiannya bertindak sebagai input untuk penggas downdraft dan fluidized untuk menghasilkan gas hidrogen dan melalui kajian ini, analisis prestasi dari segi parameter optimum dan komposisi pengeluaran gas kemudiannya dijalankan. Di sini udara digunakan sebagai bahan tindak balas input untuk penggas downdraft manakala penggas fluidized menggunakan stim untuk proses pengegasan ini. Dalam projek ini, pengesahan model yang dilakukan dahulu di mana data komposisi gas yang diperolehi daripada model keseimbangan termodinamik menunjukkan persamaan dengan hasil eksperimen dari Zainal et al. (2001) untuk penggas downdraft menggunakan kayu dan Karmakar dan Datta (2011) untuk penggas fluidized menggunakan sekam padi. Selepas itu analisis prestasi dilaksanakan untuk menyiasat parameter optimum untuk penggas downdraft dan fluidized. Berdasarkan analisis ini, parameter optimum diperolehi adalah pada suhu 770^0C dengan kandungan lembapan sebanyak 0.2 dan stim dengan biomas rasio 1.32, gas hidrogen yang dihasilkan daripada kayu, sekam padi, habuk papan dan buah tandan kosong dalam penggas downdraft adalah masing-masing 16,38%, 17,02%, 16.30% dan 50,12% , manakala di penggas fluidized masing-masing adalah 38,75%, 50,00%, 73,24% dan 71,77%. Hasil analisis prestasi menunjukkan bahawa penggas fluidized adalah lebih cekap daripada penggas downdraft dari segi pengeluaran gas hidrogen.

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LIST OF ABBREVIATIONS

C	Carbon
CH_4	Ethane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
Cp	Heat Capacity
EFB	Empty Fruit Bunch
G	Gas phase
H_2	Hydrogen
H_2O	Water
HHV	High Heating Value
L	Liquid phase
LHV	Low Heating Value
MC	Moisture Content
O_2	Oxygen
P	Pressure
R	Universal gas constant
T	Temperature
Tam	Ambient Temperature
ΔH	Enthalpy change

1 INTRODUCTION

1.1 Motivation, problem statement and brief review

Energy is an essential source for application in domestic and industrial activities. However, the energy production and usage can lead to environmental, economic and social impacts. The production of energy through combustion of fuel like coals normally lead to the problem of global warming caused by the rapidly increasing emissions of greenhouse gases such as carbon dioxide (CO_2) and methane.

Previously, one of the approaches to produce energy is by burning coals through combustion or gasification processes (Boqiang and Ouyang, 2014). The combustion and gasification processes utilizing coal leads to the increased carbon dioxide emissions and over ash accumulation which leads to the greenhouse effect (Salleh et al., 2009). The coal is one of the types of fossil fuels which is non-renewable type of fuels. Therefore, the coal can be short-run sometimes in the future and also affecting the environment through the mass production of carbon dioxide. Since some of the electric utilities are consumed of fossil fuels from the coal, therefore an alternative for the energy production is then necessary (Patrik, 2001).

Increasing of global concern on the environmental issues and decreasing the dependence to the fossil fuels leads to the use of renewable energy (Galindo et al., 2014). Renewable energy becomes an alternative energy technologies which use feed stocks like biomass, biogas or, solar to meet the future energy demand (Galindo et al., 2014). It will not give adverse effect on the environment when compare to the fossil fuels (Canbing et al., 2014).

Currently, enormous efforts have been done to recycle waste materials to produce energy where the major proportions of waste materials are the biomass materials. Gasification process is not a new technology but it is quite new technology for most of the peoples and thus, the introduction of the technology requires research to identify the potential benefits, and the potential risks to convince people to use this type of technology. For the analysis, there is a need to consider a detail characteristics and potential of the technology which may include the amount of energy can be produced from the production and the effect of any condition change on the energy production rate.

Biomass becomes one of the most promising renewable energy sources due to its abundance, energy content, and the low emissions of carbon dioxide to the atmosphere (Gao et al., 2008). Usually, the energy from biomass materials may come from plant sources, such as wood from natural forests, waste from agricultural, forestry processes and industrial or human and animal wastes (Twidell, 1998). Biomass gasification produces syngas through thermo chemical conversion of biomass, usually involving partial oxidation of feedstock in the presence of air, oxygen or steam (Li et al., 2004). In Malaysia particularly, the biomass materials such as wood, rice husk, empty fruit bunch and sawdust are cheap abundant resources and therefore can be utilized for energy production using biomass gasification process. Here, the biomass gasification is one of the approaches to convert these biomass materials to energy where it is an attractive solution to solve both waste disposal and energy problems by producing fuel gas like hydrogen (Karmakar and Datta, 2011). Hydrogen is one of the clean energy sources and a potential alternative fuel. The combustion of hydrogen does not negatively affect the environment.

Nowadays, many gasification technologies to exploit biomass abundances such as downdraft and fluidized bed gasifier are used to produce of electricity, heat, chemicals and liquid fuels. Technically, there are two groups of biomass gasification models to represent downdraft or fluidized bed gasifications which are equilibrium approach and kinetic approach. Kinetic models predict the progress and product composition at different positions along a reactor, whereas equilibrium model predicts the maximum achievable yield of a desired product from a reacting system (Li et al., 2004).

Kinetic models concern on the chemical kinetics of the main reactions and the transfer phenomena among phases, estimating the composition of each species on any point of space and time of a system. The kinetics models are specified in general for each process by providing important considerations on the chemical mechanisms and to increase the reaction rates and the overall process performance. However, the kinetic models always contain parameters which make them hardly applicable to different plants (Schuster et al., 2001). An accurate description of the chemical kinetic rate expression is a key issue. The choice of chemical kinetic laws is difficult because there are as many kinetic laws as kinetic studies. A large discrepancy can be observed between them and it is highly hazardous to extrapolate literature results obtained under different operating conditions (Avdhesh, 2008). For example, the steam and carbon dioxide reforming reactions of char are kinetically limited at temperatures lower than 1000 ℃ (Koroneos and Lykidou, 2011).

Although kinetic models provide essential information on mechanisms and rates, equilibrium models are more suitable as it can predict thermodynamic limits to design, evaluation and improve a process. Equilibrium model also provides a useful design aid in evaluating the limiting possible behaviour of a complex reacting system which is difficult or unsafe to reproduce experimentally or in commercial operation. It provides the greatest possible conversion of each species regardless the system size and the time needed to reach equilibrium. These models do not require details of system geometry neither estimate the necessary time to reach that equilibrium (Karmakar and Datta, 2011).

The increase of global concern on environmental issues had led to the finding of alternative ways to produce energy. One of the most promising ways of energy production is through the use of renewable energy like biomass gasification process. Since the gasification models can be divided into two groups that are equilibrium approach and kinetic approach, the comparison between both types of model had been done. Among them the most effective and applicable model is the equilibrium model due to its behaviour and operation system.

1.2 Objectives

The following are the objectives of this research:

i) To investigate and analyse the performance of downdraft biomass gasification using thermodynamic equilibrium model using wood, rice husk, empty fruit bunch and sawdust.

ii) To investigate and analyse the performance of fluidized bed biomass gasification using thermodynamic equilibrium model using wood, rice husk, empty fruit bunch and sawdust.

iii) To optimize the important parameters in term of gasifier temperature, moisture content, steam biomass ratio and carbon conversion for downdraft and fluidized bed gasification.

iv) To compare the performance of downdraft and fluidized bed biomass gasification under nominal operating condition and optimal condition.

1.3 Scope of this research

The following are the scope of this research:

i) Analysis of the performance downdraft biomass gasification using thermodynamic equilibrium model using wood, rice husk, empty fruit bunch and sawdust.

ii) Analysis of the performance fluidized bed biomass gasification using thermodynamic equilibrium model using wood, rice husk, empty fruit bunch and sawdust.

iii) Optimization of the parameters in the downdraft and fluidized bed gasification for better and improved performance.

iv) Performance comparison analysis between downdraft and fluidized bed biomass gasification under nominal operating condition and optimal condition.

1.4 Main contribution of this work

The following are the contributions

a) Development a generic equilibrium thermodynamic model that is capable to apply for a wide range of biomasses
b) The optimum condition for biomass gasifier such as downdraft and fluidized bed can be determined to maximize the hydrogen production
c) Performance validation between experimental data from journal and the developed equilibrium model

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the gasification, the type of gasifier, thermodynamic equilibrium model and previous studies on biomass. For gasification part, the process and the product from gasification will be described. The comparison on the gasifier types is made and reviewed to provide the best types of gasifier to be used. Thermodynamic model will be reviewed and the model used to represent the biomass gasification is analysed. A summary of the previous work on various type of biomass give an overview on the type of biomasses used.

Chapter 3 is the explanation on the step by step on how the whole procedures were done in this work. These procedures were implemented in order to analyse the performance of gasification process.

Chapter 4 shows the excel calculation of thermodynamic model and summaries of the work done. Excel is use since it is user friendly where here user can easily make decision on the type of gasifier, type of biomass, and operating condition in order gets the composition of gas produced.

Chapter 5 is the result of performance analysis that had been done in excel sheet. In this chapter, the thermodynamic model validation is made by comparing the model data with the work in Zainal et al., (2001) for downdraft gasifier and Karmakar and Datta.,(2011) for fluidized bed gasifier. The biomass is then tested in downdraft and fluidized bed gasifier at different condition to find out the most optimum condition and most efficient biomass in both gasifier.

Chapter 6 is the conclusion of this final year project includes the overview on the previous work, objective, scope of studies, contribution, the whole procedure on how the work is to be done, the result of this analysis and the summaries of the work.

2 LITERATURE REVIEW

2.1 Overview

This paper presents the review of gasifier using different type of biomasses. The main purpose of this analysis is to review the performance of gasifier in order to facilitate the selection of the gasifier in term of the energy production. The analysis is based on many factors like type of gasifier, the biomasses used and the parameter used to test the performance.

2.2 Gasification Process

The use of the forest biomass, agricultural or animal residues as a source of energy contribute to lower energy dependency on fossil fuels and in such a way reducing greenhouse gases emissions (McKendry, 2002). Gasification is one of the ways to produce energy from the biomass. Typically, gasification is a thermo-chemical conversion technology or partial combustion process to convert biomass materials into energy through partial oxidation where solid fuel are transform into gas product (Bi and Liu, 2010). A limited amount of air that supplied to biomass gasifier will leads to burning of a relatively small part of biomass which generates heat to maintain a series of thermochemical processes. During gasification four main processes occur inside the reactor which is drying, pyrolysis, oxidation and reduction, and each of these processes has certain physical and chemical features (Felipe., 2012). During gasification process, the biomass is heated to a high temperature, which causes a series of physical and chemical changes that result in the production of volatile products and carbonaceous solid residues. The gasification process uses an agent, either air, oxygen, hydrogen or steam to convert carbonaceous materials into gaseous products. Steam may be added from an external source or from the dehydration reactions of crop residues. Compared to air gasification, steam gasification produces a higher energy based on the gas produced. (Sadaka, 2013).

The main gas produced by gasification is the synthesis gas or syngas which is a mixture of carbon monoxide, hydrogen, methane, carbon dioxide and nitrogen (Chen et al., 2007). The composition of this gas depends on several factors such as the type of biomass used in the process, the temperature and the type of gasification agent

(McKendry., 2002). The syngas can be directly used as a gaseous fuel and can be processed further to produce electricity and heat. Usually, this gas is burned to produce heat and steam or used in the gas turbines to produce electricity (Babu and Sheth., 2006). The efficiency of gasification is based on the biomass material, particle size, gas flow rate and design of the gasifier. Gasifier can be grouped based on the direction of gas flow such as updraft, downdraft, cross draft and fluidized bed (Avdhesh., 2008).

2.3 Types of Gasifier

The differences of properties in chemical, physical and morphological of biomass lead to the different methods of gasification or gasification technologies (Karmakar and Datta, 2011). The study of biomass gasification has been conducted extensively by researchers around the world. The selection of gasifier is determined by their different features. Different gasifiers have different operation mechanism. In gasifiers, as air or steam passed through the fuel bed, fairly discrete drying, pyrolysis, gasification and oxidation zones develop along the reactor. The location of these zones in the gasifier depends on the relative movement of the fuel and air (Sadaka., 2013).

Figure 2-1 illustrates the flow of the fuel and gases in the moving bed gasifier. Most of these types of gasifiers are used with oxygen and steam injected into the bottom of the reactor while the biomass material is fed at the top, producing a counter-current flow. The raw fuel gas flows relatively slowly upward through the bed of biomass feed and cools by drying the biomass. This process allows a lower syngas temperature at the output (400 ℃ -500 ℃), avoiding the needing of an expensive cooling system. Ash may be either dry or slag depending on the steam/oxygen ratio and the melting characteristics of the mineral matter. This gasifier produced syngas has a high heating value due to the high methane content and the consumption of oxygen in the reactor is very low. As a result, the thermal efficiency of the process is very high.

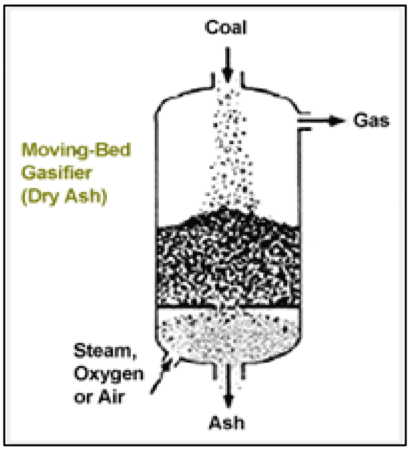

Figure 2-1: Moving Bed Gasifier (adopted from Garcia et al., 2009)

The Figure 2-2 shows the fluidized bed gasifier. There is no specific zone in the fluidized bed gasifier. Air is blown through a bed of solid particles at a sufficient velocity to keep these in a state of suspension. The fluidized bed is externally heated and the feedstock is feed after the bed reaches sufficiently high temperature. The fuel particles like gas or steam are introduced at the bottom of the reactor, very quickly mixed with the bed material and almost instantaneously heated up to the bed temperature. This fuel is pyrolysed very fast to make the component mix with a relatively large amount of gaseous materials. Further gasification and tar-conversion reactions occur in the gas phase. Most systems are equipped with an internal cyclone in order to minimize char blow-out as much as possible. Some ash particles are also carried over the top and have to be removed from the gas stream if the gas is used in engine applications.(Sadaka, 2013).

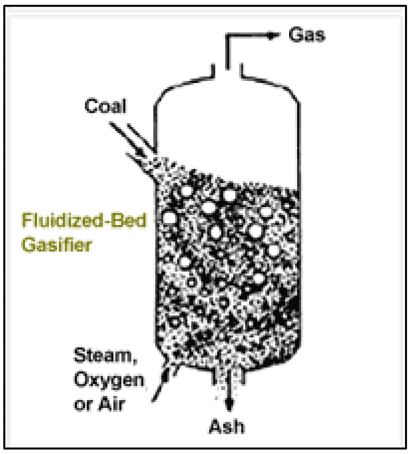

Figure 2-2: Fluidized Bed Gasifier (Adopted from Garcia et al., 2009)

Figure 2-3 illustrates the flow of the fuel and gases in the downdraft gasifier. In the downdraft gasifier, the reduction zone is located at the bottom. The high temperature oxidation zone is located at the above the reduction zone of the gasifier where part of the fuel is burned. The gasifying agent is injected at the bottom of the reactor and ascends from the bottom to the top while the feedstock is introduced at the top of the reactor and descends from the top to the bottom. The fuel descends through three zones which are drying, pyrolysis and oxidation zone of progressively increasing temperatures. The oxidation zone lies at above the injected air of the gasifier and the combustion gas passes through this zone reacting with the char produce heat. The produced gases, tar and other volatiles disperse at the top while ashes are removed at the bottom of the reactor. Part of the fuel is burned in the oxidation zone. The high tar content is not a major problem if the producer gas is used for direct heat applications. However, it requires thorough cleaning for internal combustion engine applications.

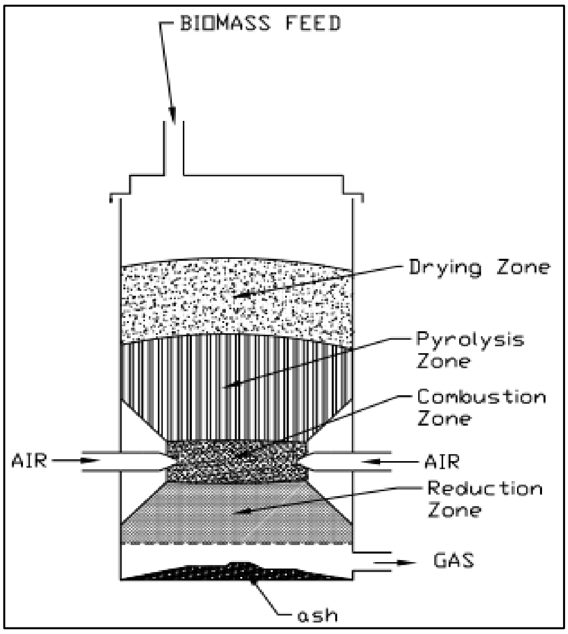

Figure 2-3: Downdraft Gasifier(adopted from Sadaka., 2013)

Table 2-1: Advantage and Disadvantages of Each Type of Gasifier.

Type of Gasifier	Advantages	Disadvantages
Moving-bed Gasifier	• Lower the pressure drop	Suffer from high tar yields inability to maintain uniform radial poor response to load change(Beenackers, 1999; Babu, 1995).
Fluidized beds Gasifier	• High Heating value (HHV) (Schuster et al., 2001). • increase the bunker flow • lower the pressure drop	poor response to load change(Kent.A.J .,

	• lower the slagging • Feedstock steam are flexible • High heat and mass transfer rates(Salleh et al., 2009).	
Downdraft Gasifier	• comparatively cheaper • produces relatively low tar during gasification • can achieve a higher hydrogen content (Giltrap et al., 2003)	High ash content(Sadaka. , 2013)

From the comparison, moving bed had less advantages and more disadvantages compare to the other gasifiers. The fluidized bed gasifier and downdraft gasifier is seems to be more applicable when compare with moving bed gasifier. The fluidized bed had poor response to load change which this problem also faced by the moving bed gasifier so it is better to choose gasifier with more advantages. The high ash content in downdraft will not be a big problem if there are consistent waste management of the remains ash.

Many researchers investigated hydrogen production from biomass gasification in a fluidized bed and only a few studies explore hydrogen-rich gas production in a downdraft gasifier (Pengmei Lva et al., 2007). More studies should be done on the downdraft since both type of gasifier has an ability of hydrogen gas production and a proper comparison between these two types of gasifier should be done to analyse the performance of these gasifier.

2.4 Thermodynamic Equilibrium Model

Traditionally, the simulation of gasifier may be carried out by thermodynamic equilibrium modelling, kinetic modelling, numerical modelling and artificial neural network (Budhathoki et al., 2013). The important parameters such as moisture content, equivalence ratio, producer gas composition and heating value of gas have been analysed in chemical equilibrium approach (Pitchandi, 2012). A mathematical model is developed to predict performance of a biomass gasifier. The model is mostly used to study of process parameters such as reactor temperature, steam biomass ratio and moisture content which generally influence the percentage of hydrogen content in the product gas (Avdhesh, 2008).

Thermodynamic equilibrium never takes place in real gasification process (Chowdhury et al., 1994) but many works demonstrate the use of equilibrium model. Researchers used the equilibrium model based on the minimization of Gibbs free energy to analyses the gasification process and also to solve the optimization and non-linear equation problems based on the gasification process. Equilibrium model can also based on the equilibrium constant. However, equilibrium model based on the minimization of Gibbs free energy and equilibrium constants are of the same concept (Li et al., 2001; Altafini et al., 2003). Some of the models have been developed based on thermodynamic and chemical kinetics to find out the temperature and rate of feedstock consumption in the pyrolysis zone (Sharma, 2008; Kaosol and Sohgrathok, 2013). Schuster et al. (2001) also developed a model for steam gasification of biomass applying thermodynamic equilibrium calculations that combined heat and power station based on a dual fluidized bed steam gasifier.

Zainal et al. (2001) used the equilibrium constant equilibrium model to predict the performance of gasifier. It was observed that the calorific value of the producer gas decreases with increase in moisture content and the gasification temperature. The amount of oxygen in that model was eliminated by defining it to some components in producer gas. This model can predict the reaction temperature by knowing the amount of oxygen, and vice versa. The coefficients determined from the comparison of the predicted results with the experimental results from other works can be multiplied with the equilibrium constants to improve the model. Equilibrium models convert species regardless of the system size and the time needed to reach equilibrium (Rodrigues et al., 2009).

From Zainal et al. (2001), the equilibrium model assumes that all the reaction are in thermodynamic equilibrium. It is expected that the pyrolysis product burns and achieves equilibrium in the reduction zone before leaving the gasifier, hence an equilibrium model can be used in the downdraft gasifier.

The reaction involve in the gasification process are as follows:

Steam gasification

$C + CO_2 = 2CO$ (1)

Boudouard reaction

$C + H_2O = CO + H2$ (2)

Methanation reaction

$C+2H_2 = CH_4$ (3)

The other important reaction involve is the steam formation reaction.

$CH_4+H_2O=CO + 3H_2$ (4)

The shift reaction of

$CO+H_2O=CO_2 + H_2$ (5)

The formula of steam formation reaction and shift reaction is then deriving into equilibrium constant for methane formation as follow:

$$K_1 = \frac{P_{CH_4}}{(P_{H_2})^2} \quad (6)$$

$$K_2 = \frac{P_{CH_4} P_{H_2}}{P_{CO} P_{H2O}} \quad (7)$$

The chemical formula is defined in term of $C_nH_aO_b$ which is based on single atom in general to develop the global gasification reaction. In the Zainal et al. (2001) the calculation was given by using the raw material of woody materials. The typical chemical formula of woody materials based on single atom of carbon is $CH_{1.44}O_{0.66}$. Thus the overall chemical reaction is represented as below:

$CH_{1.44}O_{0.66}$ +w H_2O +mO_2 +3.76m N_2 = x_1 H_2 + x_2 CO + x_3 CO_2 + x_4 H_2O + x_5 CH_4 +3.76mN_2 (8)

Where,

w is the amount of water per kmol of material

m is the amount of oxygen per kmol of material

x_1 , x_2 ,x_3 ,x_4 and x_5 is the coefficient of constituents of the products.

Here the w can be determined by using moisture content (MC) formula as shown below:

$$MC = \frac{mass\ of\ water}{mass\ of\ wet\ biomass} \times 100\% = \frac{18w}{24+18w} \times 100\%$$

Therefore,

$$w = \frac{24MC}{18(1-MC)}$$

After the moisture content is known, the value of w becomes a constant. From the global reactions, there are six unknown x_1, x_2, x_3, x_4, x_5 and m, representing the five unknown species of the product and the oxygen content for the reaction. Therefore, six equations are required, which are formulated below:

Carbon balance:

$1= x_1 + x_2 + x_3 + x_4 + x_5$ (9)

Hydrogen balance:

$2w + b= 2x_1 + 2x_4 + 4x_5$ (10)

Oxygen balance:

$w + a +2m = x_2 + 2x_3 + x_4$ (11)

Equilibrium constant from methane formation (Equation (6)):

$K1=\frac{x_5}{x_1^2}$ (12)

Equilibrium constant from shift reaction (Equation (7)):

$K2 = \frac{x_1 x_3}{x_2 x_4}$ (13)

In order to find the value for the unknown most of the equation had been derived in term of heat change in term of temperature. The first stage of derivation is to find the value of K_1 and K_2 in term of temperature.

The heat of formation equation for the formation of 1mol of solid biomass ($CH_{1.44}O_{0.66}$) from solid carbon, hydrogen and oxygen is:

$C_{(sol)} +0.72\ H_{2\ (g)} + 0.33O_2 \longrightarrow CH_{1.44}O_{0.66}$ (14)

and in the reality, the reaction cannot occur. The formation of $CH_{1.44}O_{0.66}$ is based on the following reactions:

$C + O_2 \longrightarrow CO_2$ ΔH_c= -393509

$0.72\ H_2 +0.36\ O_2 \longrightarrow 0.72\ H_2O$ ΔH_c= -241818 x(0.72)

$CO_2 + 0.72\ H_2O \longrightarrow CH_{1.44}O_{0.66} + 2.06\ O_2$ ΔH_c= 449568

$C + 0.72\ H_2O + 0.33\ O_2 \longrightarrow CH_{1.44}O_{0.66}$ ΔH_f =-118050 kJ/kmol

Therefore, the heat of formation of materials is -118050kJ/kmol. Hence, the heat of formation for any biomass material can be determined if the ultimate analysis and the heating values of the material are known. The heating value can be determined experimentally by bomb calorimeter, the heat of formation of any biomass material can be calculated with good accuracy from the following:

ΔH_c =HHV (kJ/kmol) =0.2326(146.58 C+56.878 H -51.53 O - 6.58 A + 29.45) (15)

Where C, H, O, and A are the mass fractions of carbon, hydrogen, oxygen and ash, respectively, in the dry biomass. The chemical formula of any biomass material can be determined if the ultimate analysis is known. At constant pressure, the specific heat can be written as:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{16}$$

Or

$$dH = C_p dT \tag{17}$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT \tag{18}$$

Where H is the enthalpy and T is the temperature.

Equation (18) can be written as

$$\Delta H = C_{pmh} (T_2 - T_1) \tag{19}$$

Where C_{pmh} is the average specific heat over the temperature change $\Delta T = T_2 - T_1$ with T_2 is the gasification temperature at reduction zone and T_1 is the ambient temperature at the reduction zone.

$$C_{pmh} = \left(\frac{\int_{T_1}^{T_2} C_p dT}{T_2 - T_1}\right) \tag{20}$$

The dependence of specific heat on the temperature is given by an empirical equation and the most simplified version is:

$$C_{pmh} = R\left(A + BT_{am} + C/3\,(4T_{am}^2 - T_1T_2) + \frac{D}{T_1T_2}\right) \tag{21}$$

Where $T_{am} = (T_1 + T_2)/2$ is the arithmetic mean temperature and R is the universal gas constant (8.314 J/mol K).The constant A, B, C and D for Cp is taking from the Smith et al. (2005). The enthalpy changes, ΔH, can be obtained using Equation (19). The equilibrium constant K is a function of temperature only and is written as follows:

$$-RT\ln K = \Delta G^0, \tag{22}$$